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# PATENT SPECIFICATION

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Int. Cl.:—C 08 f 27/00 // B 44 d, D 04 j

## COMPLETE SPECIFICATION

### Improvements in and relating to Adhesives

We, MONSANTO COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of 800 North Lindberg Boulevard, St. Louis, Missouri, United States of America, (assignee of DAVID VERNON COLLINS), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to nonwoven fabrics bonded with polyvinyl acetate. More particularly, the present invention relates to the binding of said fabrics by the use of aqueous emulsions of partially hydrolyzed polyvinyl acetate which can be crosslinked in the fabric.

The use of polyvinyl acetate resin to bind randomly distributed fibres and filaments into nonwoven fabrics is known. Fabrics so bonded, however, have seen their utility rather seriously limited by the inability of polyvinyl acetate to withstand any pronounced exposure to water; under such conditions the binder polymer suffers a significant loss of strength and adhesiveness. Any successful treatment therefore which would restore this low cost and otherwise very acceptable resin to its full potential utility through an increase in its water resistance while retaining its applicability in the form of aqueous emulsions, would be very welcome by the trade.

The problem has been approached in various manners. Polyvinyl acetate has been hydrolyzed, completely or partially, and the resulting product crosslinked with many hydroxyl reactive materials. These treatments however, while ultimately achieving the goals of water resistance, cold flow reduction and non-blocking, have meant the sacrificing of

the convenience of application of the resin as an aqueous emulsion. Other efforts have been directed to the combining of polyvinyl acetate emulsions with thermosetting resins. Some improvement in properties has been achieved in this manner, probably through the crosslinking of hydroxyl-bearing emulsifiers and protective colloids present in the emulsions. But strikingly better results can be obtained when the polyvinyl acetate itself can be made to participate in this crosslinking reaction.

For these reasons, the binding of fibres and filaments into water-resistant nonwoven fabrics has remained heretofore within the province of other crosslinkable agents such as the natural and synthetic rubbers, various acrylics of undisclosed compositions and hydroxyethyl acrylate copolymers. In the more general fields of surface coating and adhesives, hydroxyl-containing polymers are also available, the hydroxyl groups being introduced in the molecules by copolymerization with hydroxyl-bearing vinyl monomers. In all such cases, there exist problems created by difficulty in polymerization, high cost of monomers as compared to vinyl acetate and often, relatively poor availability of hydroxylated comonomers.

The present invention contemplates the provision of fibrous products bonded with a cross-linked polyvinyl acetate resin. It contemplates further the provision of aqueous emulsions of polyvinyl acetate which can be crosslinked to give a water-resistant non-blocking cured product having reduced cold flow.

This may be effected by treating polyvinyl acetate emulsions with an hydrolysis catalyst under conditions such that 0.5 to 13% of the acetate groups present are converted to hydroxyl groups. The resulting products are then compounded with a compatible hydroxyl-

[Price 4s. 6d.]

reactive crosslinking agent. On application of these formulations to nonwoven webs in the customary manner and upon suitable curing, nonwoven fabrics are obtained which possess excellent wash resistance, withstanding at least ten machine washings with no adverse effects.

According to the present invention therefore there is provided an adhesive composition comprising an aqueous dispersion of a partially hydrolyzed water-dispersible homopolymer or copolymer of vinyl acetate containing from 1 to 6% by weight of hydroxyl groups calculated as polyvinyl alcohol and a water-dispersible polyfunctional hydroxyl-reactive compound in an amount ranging from 2 to 25% by weight of the polymer.

The present invention also provides a substrate particularly a non woven fibrous product having an adhesive thereon or therein comprising the reaction product of a partially hydrolyzed water-dispersible homopolymer or copolymer of vinyl acetate containing from 1 to 6% by weight of hydroxyl groups calculated as polyvinyl alcohol and a water-dispersible polyfunctional hydroxyl-reactive compound in an amount ranging from 2 to 25% by weight of the polymer; said polymer being crosslinked to the extent that it is insoluble in polyvinyl acetate solvents, cannot be heat sealed below 300°F. and is substantially water insensitive.

In a further embodiment thereof the present invention provides a process for the production of the aforesaid substrate which comprises applying thereto the aforesaid adhesive and drying and curing the product at a temperature from 220 to 350°F.

The emulsions which may be used in this invention are those aqueous dispersions of the homopolymers and copolymers of vinyl acetate that are stable in the presence of mineral acid or can be made so stable by the incorporation of additional emulsifier or protective colloid. Where a copolymer is employed, the comonomers include for example dibutyl maleate, 2-ethylhexyl acrylate, ethyl acrylate, acrylic acid and crotonic acid. Emulsions which may be used are those having a solids content ranging from 10 to 60% by weight, a pH from 3 to 6, and a Brookfield viscosity within the range of 25 to 4500 centipoises at 25°C. The polymers in these emulsions should preferably have a number average molecular weight of from 10,000 to 500,000 and an average particle diameter of 5 microns or less.

The preferred emulsions are those of homopolymers and copolymers of vinyl acetate having a solids content of 40 to 60% by weight, a Brookfield viscosity ranging from 300 to 3000 centipoises at 25°C., an average particle diameter of one micron or less and a pH from 3 to 6. Particularly useful are those emulsions of polyvinyl acetate in which the resin has been made to react chemically during

its formation with a solid block copolymer of ethylene oxide and propylene oxide.

The most preferred vinyl acetate polymer is a homopolymer of vinyl acetate which has a number average molecular weight of 35,000 and an average particle size of 0.2 to 0.3 microns.

The partial hydrolysis of these polymers can be accomplished by a catalyst that is either acidic or basic. An acid catalyst is preferred however since it is not neutralized in the course of the reaction by the acetic acid liberated, as is the case with an alkaline catalyst. The concentration of the catalyst can be varied from 0.25 to 3% by weight of the resin solids. The potential upper limit of concentration is the point at which the acid causes the resin to coagulate. At the higher concentrations however, colour formation becomes a problem and yet the hydrolysis rates are not greatly increased. Among the acids that may be used are hydrochloric acid, sulphuric acid, nitric acid, phosphoric acid, trichloroacetic acid, paratoluenesulphonic acid, strongly acidic ion-exchange resins and formic acid. It is preferable to employ these acids in dilute concentrations, say as 6N solutions. The actual selection of the acid to be used in a particular preparation and the actual amount employed within the limits already mentioned are also influenced by the nature of the container in which the hydrolysis is carried out, the time allowable for the reaction, the temperature and the particular emulsion treated, i.e. the nature of the polymer and its particle size. As to the use of basic catalysts such as sodium hydroxide, there is a problem of maintaining the hydrolysis pH selected for the particular emulsion by addition of more alkaline solution as it becomes neutralized by acid liberated during the hydrolysis. It should be noted however that alkaline hydrolysis is more rapid than acid hydrolysis and must therefore be controlled more carefully.

Hydrolysis temperature can be varied over a wide range. The temperatures used were from 45 to 95°C. As expected, hydrolysis rates increase at higher temperatures but skin formation, emulsion instability and colour formation minimize the former advantage. The preferred temperature range is from 50 to 90°C.

The time of hydrolysis is, as can be expected, a function of the acid selected, the concentration used, the nature of the polymer, the particle size of the dispersed resin and the temperature employed. It can vary widely under the influence of those factors. Its empirical determination for each preparation does not present any difficulty.

The crosslinkability of the hydrolyzed emulsion polymer varies with the degree of hydrolysis. Usable emulsions are those in which from 0.5 to 13% by weight of the acetate

groups of the polymer have been hydrolysed which is equivalent to a polymer containing approximately from 1 to 6% hydroxyl groups calculated as polyvinyl alcohol. Preferably the polymer contains 3 to 6% by weight hydroxyl groups, calculated as polyvinyl alcohol. Within these limits, the actual extent of hydrolysis carried out on a polymer will depend on the use intended for the product. For instance, in order to obtain the desirable increase in resistance to washing in a nonwoven fabric, a 6 to 13% by weight degree of hydrolysis is preferred. For other applications, lower or higher degrees of hydrolysis may prove satisfactory, but as shown in the following Table II, a practical limit is soon reached on the higher side due to increase in emulsion viscosity, gelling and, ultimately, solution of the polymer.

As to usable crosslinking agents, any polyfunctional, hydroxyl-reactive type of compound may be employed under the proper conditions. A list of these types includes amino-plasts phenolic resins, di- and polyisocyanates, divinyl sulphones, epoxy resins and dialdehydes. The choice rests on such considerations as economy, properties and the type of curing facility and technique available. Specific examples of usable crosslinking agents are dimethylolethyleneurea, dimethylolurea, trimethylol melamine, blocked polyisocyanates such as the phenol adduct of tolylene diisocyanate, and glyoxal.

The concentrations of crosslinking agent can be varied over a wide range. Useful limits can be set at 2 to 25% by weight, based on the total emulsion solids. While 2% will be sufficient to crosslink the partially hydrolyzed polyvinyl acetate as a free film, that amount would not be satisfactory in a nonwoven fabric where the crosslinking agent reacts not only with the resin but also with the fibres. This reaction is of course beneficial in that it brings about a certain amount of bonding between the fibres and the binder but, on the other hand, it increases the requirement of crosslinking agent. In such applications 8 to 20% concentrations have given good results.

Curing, i.e. crosslinking, takes place preferably at temperatures ranging from 220° to 350°F. The time of cure will vary with the crosslinking agent used, the particular polymer selected and the temperature. In general a period of not more than 10 minutes should suffice.

Polyvinyl acetates resins crosslinked in this manner will not be heat sealed at temperatures lower than 300°F. Other improvements, include a remarkable increase in water resistance of the polyvinyl acetate and a reduction of the cold flow property.

Application of these compounded partially hydrolyzed emulsions to substrates is carried out by conventional methods. These include spraying, foam coating, roller coating and

calendering, dip coating and simple spreading followed by scraping with a doctor blade.

Substrates of particular interest are nonwoven fibre mats made with cellulosic fibres such as cotton, viscose and rayon or with polyamides, polyesters or polyvinyl resins. Mixtures of these fibres may also be used. In this type of operation, the binder emulsions should be applied in such concentration and manner that the final resin content of the manufacture ranges from 10 to 200% of the total fibre weight. Most satisfactory results are obtained when the amount of resin binder in the finished fabric is equal to 25 to 100% of the fibre weight.

While the crosslinkable polyvinyl acetate emulsions have been developed primarily for use as nonwoven fabric binders, it will be obvious that their usefulness is not limited to this application. As will be shown the emulsions may be employed successfully in coating metallic panels. In general, it may be stated that the materials, techniques and variations described in this invention should be of value wherever the water sensitivity of an untreated vinyl acetate polymer applied as an emulsion is a disadvantage. The possibilities encompass the fields of textile finishing, paper coating, adhesives and surface coating generally.

The present invention will be further illustrated by way of the following examples.

#### EXAMPLE I

The basic emulsion employed in this example is a commercial product marketed as Gelva Emulsion TS-85 (GELVA is a Trade Mark) by the Shawinigan Resins Corporation. It can be characterized as follows: It is a mineral acid stable aqueous dispersion of a homopolymer of vinyl acetate. The particular batch employed here has a pH of 5.0, a solids content of 55% by weight, an average particle diameter of 0.2 to 0.3 micron, a molecular weight (number average) of 30,000 to 40,000 and a viscosity of 1800 centipoises at 25°C.

This emulsion, 727 g., was stirred mildly while 18 ml of 6N hydrochloric acid (4 g HCl) was added dropwise. The mixture was placed in an oven at 50°C. for 47 hours, then cooled to room temperature and neutralized with 26 ml. of 6N sodium hydroxide. Infra-red analysis showed that about 12% of the acetate groups of the homopolymer had been converted to hydroxyl groups.

#### EXAMPLE II

To 10 g of the partially hydrolyzed polyvinyl acetate emulsion of Example I was added 0.5 ml of dimethylolethyleneurea and 0.25 ml 2-amino-2-methyl-propanol hydrochloride. A film cast on an aluminium panel from this mixture and cured at 150°C. for 2 minutes was insoluble in methanol and acetone and did not heat seal below 350°F. In contrast,

a film similarly cast from a nonhydrolyzed TS—85 emulsion compounded with the same crosslinking agent and catalyst and cured in the same manner was soluble in methanol and acetone and could be heat sealed at 150 to 175°F.

### EXAMPLE III

To 80 g of the partially hydrolyzed TS—85 emulsion of Example I was added 16 g dimethylethyleneurea, 4 ml 2-amino-2-methyl-propanol hydrochloride and 300 g water. An 85:15 viscose-cotton two-ply carded web weighing about 1.2 ounces per square yard was saturated with the emulsion and passed between squeeze rolls adjusted to give a wet pick-up of about 500%. The web was dried at 150°C. for 5 minutes. The resulting nonwoven fabric had a binder-fibre ratio of approximately 38:62.

The nonwoven fabric was laundered in an automatic home washing machine. It remained undamaged after ten washings under the following conditions: 140°F. water, ordinary commercial detergent and a 20 minute wash cycle followed by spin-drying and ironing.

Nonwoven fabric prepared and treated according to the above procedure, but without the benefit of the partial hydrolysis, of the polymer completely disintegrated on one to

three washings and ironings, even when the crosslinking agent was used.

### EXAMPLE IV

A polyvinyl acetate emulsion (Gelva TS—85), 1000 g, was stirred gently in a two-litre glass vessel maintained at 83°C. + 1°C. in a thermostatted water bath. A quantity of 25 ml 6 N hydrochloric acid (5.5 g HCl) was added gradually over a period of 15 minutes. Moderate agitation was continued for 4 hours. The emulsion was then neutralized with 25 ml 6N sodium hydroxide. About 10% of the acetate groups of the homopolymer were converted to hydroxyl groups according to infra-red analysis.

As in Example II, the resulting emulsion could be crosslinked with dimethylethyleneurea to give, on application to aluminium panel and curing, a film which was resistant to solvents and had an elevated heat seal temperature.

The partially hydrolyzed emulsion was compounded with dimethylethyleneurea and used as a nonwoven fabric binder in the manner described in Example III. Fabrics so prepared withstood ten consecutive washings and ironings without apparent damage.

The physical properties of the initial and partially hydrolyzed emulsions are summarized in the following table.

TABLE I

Property	Emulsion		
	Original	Hydrolyzed	Compounded
% Solids	55	51	51
Emulsion viscosity*	1800 cps	280	104
Mechanical stability**	good	good	good
pH	5.0	3.1	3.3
Shelf life***	good	good	good

\* Brookfield, No. 3 spindle at 30 r.p.m., 25° C.

\*\* 300 ml. of emulsion at 5% solids, sheared in Waring Blendor at 60° C. for three minutes.

\*\*\* No viscosity increase, no settling, no skin formation, etc., for at least two months.

### EXAMPLES V—XI

These examples were designed to show the relationship between the degree of hydrolysis of the polyvinyl acetate and the wash resistance of fabrics bonded therewith.

In all cases, the polyvinyl acetate emulsion was hydrolyzed with 1% by weight sulphuric

acid (all percentages here being based on the solids content of the emulsions) at a temperature of 89°C. + 1°C. and the hydrolyzed products were compounded, before application to the web, with 20% by weight of dimethylethyleneurea and 2% by weight of 2-amino-2-methyl-propanol hydrochloride.

The following table summarizes the results obtained by varying the time of hydrolysis and thereby the degree of hydrolysis of various preparations.

TABLE II

Ex.	Hydrolysis		Viscosity (cps)	Heat Seal Temperature	Nonwoven Fabric Wash Resistance	
	Time	% PVOH			Damage	Destruction
					(No. of washes)	
V	0.25	0	1120	210°F.	1	1—2
VI	2.90	2.5	280	365	3	5—10
VII	4.00	3.6	280	400	4	10
VIII	4.50	4.1	260	380	6	10
IX	5.00	4.0	1320	380	8	10
X	5.15	5.2	2400	410	10	10
XI	5.50	5.5	10000	410	10	10

The "% PVOH" given in this table is the amount of polyvinyl alcohol present in 100 g of the total solid resin after hydrolysis. It was calculated from the amount of acid formed by the hydrolysis as determined by titration of 10 g aliquots of the emulsion with dilute sodium hydroxide.

As evidenced by the results presented in Table II, the most useful degree of hydrolysis is that which yields a resin containing about 5% by weight of polyvinyl alcohol. A lower degree of hydrolysis does not achieve the wash resistance sought in the nonwoven fabrics while greater hydrolysis creates problems of viscosity, increased cost and ultimately gelling and solution of the dispersed copolymers.

## EXAMPLE XII

A commercially available vinyl acetate-dibutyl maleate emulsion (Gelva TS—71 was employed in this example. The product is further identified as follows: pH, 4.5; solids, 55% by weight; emulsion viscosity, 1320 centipoises at 25°C. (Brookfield, No. 3 spindle at 30 r.p.m.); average particle diameter, less than 1 micron; polymer viscosity (as 1 molar benzene solution at 20°C.), 15 cps.; monomer weights ratio, vinyl acetate-dibutyl maleate 3:1.

The emulsion, 800 g, was stirred gently in a two-litre glass vessel maintained at 55°C.  $\pm$  1°C. in a thermostatted water bath. A quantity of 16 g of a solid block copolymer of ethylene oxide and propylene oxide (Pluronic

F—68 (PLURONIC is a Trade Mark) ethylene oxide content; 80% by weight; hydrophobic base molecular weight, 1750) was added. Sulphuric acid, 10 ml of 10N concentration, was fed in dropwise over a period of 15 minutes. Moderate agitation was maintained for an additional period of 6 hours at constant temperature. The emulsion was then neutralized with 10 ml of concentrated ammonium hydroxide. Titration of the acetic acid released during the hydrolysis indicated the conversion of approximately 6% of the acetate groups to hydroxyl groups.

When compounded with dimethylethyleneurea and 2-amino-2-methyl-propanol hydrochloride, applied as a binder on nonwoven web and cured, all in the manner described in Example III, a nonwoven fabric was obtained which withstood ten consecutive washings and ironings without apparent damage.

## EXAMPLES XIII—XV

These examples are given to illustrate the effect of various concentrations of a cross-linking agent in the binder emulsions of this invention. In all cases, a TS—85 type homopolymer emulsion was used which was hydrolyzed to the extent that the polymer contained 5% "polyvinyl alcohol" (PVOH). The crosslinking agent was dimethylethyleneurea (DMEU) and the catalyst, 2-amino-2-methyl propanol hydrochloride (AMP). The particular concentrations studied and the results obtained upon application to nonwoven fabrics are given in the following table.

TABLE III

Ex.	Hydrolyzed TS-85 (5% PVOH) (g. solids)	DMEU (g. solids)	AMP (g)	Nonwoven fabric washes		Heat Seal temperature (free film)
				Damage	Destruction	
XIII	50	5.0	1.0	10	10	370°F.
XIV	50	2.5	1.0	4	10	365
XV	2.5	0.05	0.05	1	1-2	355

## EXAMPLES XVI AND XVII

These preparations were carried out exactly as in Example XIII, i.e. using the partially hydrolyzed TS-85 emulsion compounded with 10% by weight, based on the solids con-

tents, of crosslinking agent and 2% by weight of catalyst. The only significant change consisted in substituting for the dimethylol-ethyleneurea the other hydroxyl reactive agents shown in the next table.

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TABLE IV

Ex.	Crosslinking Agent	Cure temp.	Nonwoven fabric washes		Heat Seal temperature (free film)
			damage	destruction	
XVI	trimethylol melamine	150° C.	10	10	400°F.
XVII	phenol adduct of tolylene diisocyanate	175° C.	10	10	400°F.

## WHAT WE CLAIM IS:—

1. An adhesive composition comprising an aqueous dispersion of a partially hydrolyzed water-dispersible homopolymer or copolymer of vinyl acetate containing from 1 to 6% by weight of hydroxyl groups calculated as polyvinyl alcohol and a water-dispersible polyfunctional hydroxyl-reactive compound in an amount ranging from 2 to 25% by weight of the polymer.
2. A composition as claimed in claim 1 in which the polymer has a number average molecular weight of from 10,000 to 500,000 and an average particle diameter of 5 microns or less.
3. A composition as claimed in any of the preceding claims in which the dispersion has a solids content from 10 to 60% by weight; a pH from 3 to 6 and a Brookfield viscosity from 25 to 4500 centipoises at 25°C.
4. A composition as claimed in claim 1 or 2 in which the dispersion has a solids content of 40 to 60% by weight; a Brookfield viscosity from 300 to 3000 centipoises at 25°C, an average particle diameter of 1 micron or less and a pH from 3 to 6.
5. A composition as claimed in any of the preceding claims wherein the vinyl acetate polymer employed is a homopolymer of vinyl

acetate which has a number average molecular weight of 35,000 and an average particle diameter of 0.2 to 0.3 microns.

6. A composition as claimed in any of claims 1 to 4 in which the vinyl acetate copolymer is a copolymer of vinyl acetate with dibutyl maleate, 2-ethyl hexyl acrylate, ethyl acrylate, acrylic acid or crotonic acid.

7. A composition as claimed in any of the preceding claims in which the vinyl acetate polymer is one which has been made during its formation to react with a solid block copolymer of ethylene oxide and propylene oxide.

8. A composition as claimed in any of the preceding claims in which the hydroxyl reactive compound is an aminoplast; a phenolic resin, an isocyanate; a divinyl sulphone, an epoxy resin or a dialdehyde.

9. A composition as claimed in any of the preceding claims in which the hydroxyl-reactive compound is dimethylethyleneurea, dimethylolurea, trimethylol melamine or a phenol adduct of tolylene diisocyanate.

10. A composition as claimed in any of the preceding claims in which the hydroxyl reactive compound is present in an amount from 8 to 20% by weight of polymer.

11. An adhesive composition according to



claim 1 substantially as hereinbefore described with reference to and as illustrated in any of the Examples.

12. A substrate having an adhesive thereon or therein comprising the reaction product of a partially hydrolyzed water-dispersible homopolymer or copolymer of vinyl acetate containing from 1 to 6% by weight of hydroxyl groups calculated as polyvinyl alcohol and a water-dispersible polyfunctional hydroxyl-reactive compound in an amount ranging from 2 to 25% by weight of the polymer; said polymer being crosslinked to the extent that it is insoluble in polyvinyl acetate solvents, cannot be heat sealed below 300° F and is substantially water insensitive.
13. A substrate as claimed in claim 12 which is a metal plate.
14. A substrate as claimed in claim 12 which is a non-woven fibrous product the fibres of which are held together by 10 to 200% by weight of the adhesive based on the weight of the fibres.
15. A substrate as claimed in claim 13 in which the fibres are cellulosic, polyamide, polyester or vinyl resin fibres.
16. A substrate as claimed in claim 14 or 15 in which the amount of adhesive is from 25 to 100% by weight based on the weight of the fibres.
17. A substrate as claimed in any of claims 12 to 16 in which the polymer has a number average molecular weight of from 10,000 to 500,000 and an average particle diameter of 5 microns or less.
18. A substrate as claimed in any of claims 12 to 17 in which the vinyl acetate polymer employed is a homopolymer of vinyl acetate which has a number average molecular weight of 35,000 and an average particle diameter of 0.2 to 0.3 microns.
19. A substrate as claimed in any of claims 12 to 17 in which the vinyl acetate copolymer is a copolymer of vinyl acetate with dibutyl maleate, 2-ethyl hexyl acrylate, ethyl acrylate, acrylic acid or crotonic acid.
20. A substrate as claimed in any of claims 12 to 19 in which the vinyl acetate polymer is one which has been made during its formation to react with a solid block copolymer of ethylene oxide and propylene oxide.
21. A substrate as claimed in any of claims 12 to 20 in which the hydroxyl reactive compound is an aminoplast; a phenolic resin; an isocyanate; a divinyl sulphone, an epoxy resin or a dialdehyde.
22. A substrate as claimed in any of claims 12 to 21 in which the hydroxyl-reactive compound is dimethylolethyleneurea, dimethylolurea, trimethylol melamine or a phenol adduct of tolylene diisocyanate.
23. A substrate as claimed in any of claims 12 to 22 in which the hydroxyl reactive compound is present in an amount from 8 to 20% by weight of polymer.
24. A substrate as claimed in any of claims 12 to 23 in which the vinyl acetate polymer contains 3 to 6% by weight hydroxyl groups, calculated as polyvinyl alcohol.
25. A substrate as claimed in any of claims 12 to 24 in which the vinyl acetate polymer is a partially hydrolyzed water-dispersible copolymer of vinyl acetate and dibutyl maleate having the following characteristics: monomer weight ratio, 3:1, average particle diameter, less than 1 micron; polymer viscosity, 16 centipoises for a one molar benzene solution at 20°C.
26. A substrate as claimed in claim 12 substantially as hereinbefore described with reference to and as illustrated in any of the Examples.
27. A process for making a substrate as claimed in any of claims 12 to 26 which comprises applying to the substrate an adhesive as claimed in any of claims 1 to 11 and drying and curing the product at a temperature ranging from 220 to 350°F.
28. A process as claimed in claim 27 in which the vinyl acetate polymer contains 3 to 6% by weight hydroxyl groups, calculated as polyvinyl alcohol.
29. A process as claimed in claim 27 or 28 wherein the aqueous emulsion is one in which the vinyl acetate polymer has been partially hydrolyzed by a dilute solution of a strong acid.
30. A process as claimed in claim 29 wherein the polymer has been hydrolyzed with dilute hydrochloric acid, sulphuric acid, phosphoric acid, trichloroacetic acid, nitric acid or para-toluenesulphonic acid.
31. A process as claimed in any of claims 27 to 30 in which the aqueous dispersion comprises a vinyl acetate homopolymer emulsion having a solids content of 55% by weight, a number average molecular weight of 35,000, an average particle diameter of 0.2 to 0.3 microns and an hydroxyl group content of 3 to 6%, calculated as polyvinyl alcohol, obtained by hydrolysis with dilute sulphuric acid.
32. A process for the production of a substrate as claimed in any of claims 12 to 26 substantially as hereinbefore described with reference to and as illustrated in any of the Examples.

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